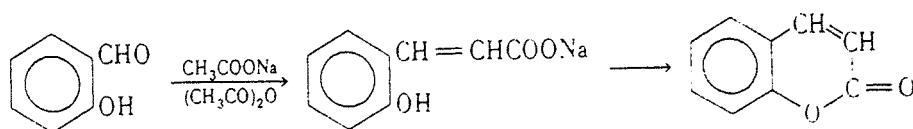


semisynthetics. Examples are vanillin, prepared from eugenol from clove oil; ionone, from citral from lemon grass oil; and terpineols, from turpentine and pine oil. Some of the significant synthetics are discussed below. The examples presented are grouped under the most important chemical conversion.

Condensation Processes⁶ (Fig. 1.1). Coumarin occurs in tonka beans and 65 other plants, but the economical source is the synthetic. It is employed as a fixative and enhancing agent for essential oils and tobacco products, and as a masking agent for disagreeable odors in industrial products. The synthetic product may be prepared⁷ in a number of different ways. One method utilizes the Perkin reaction:



Salicylaldehyde, acetic anhydride, and sodium acetate are refluxed at 135 to 155°C. The reaction mixture is cooled and washed. The coumarin is recovered by solvent extraction or distillation. Other important methods of coumarin preparation utilize *o*-cresol as the starting

⁶Process-Studded Plant: Key to Fragrance, *Chem. Eng.* 65 (4) 112 (1958).

⁷ECT, 3d ed., vol. 7, 1979, p. 196.

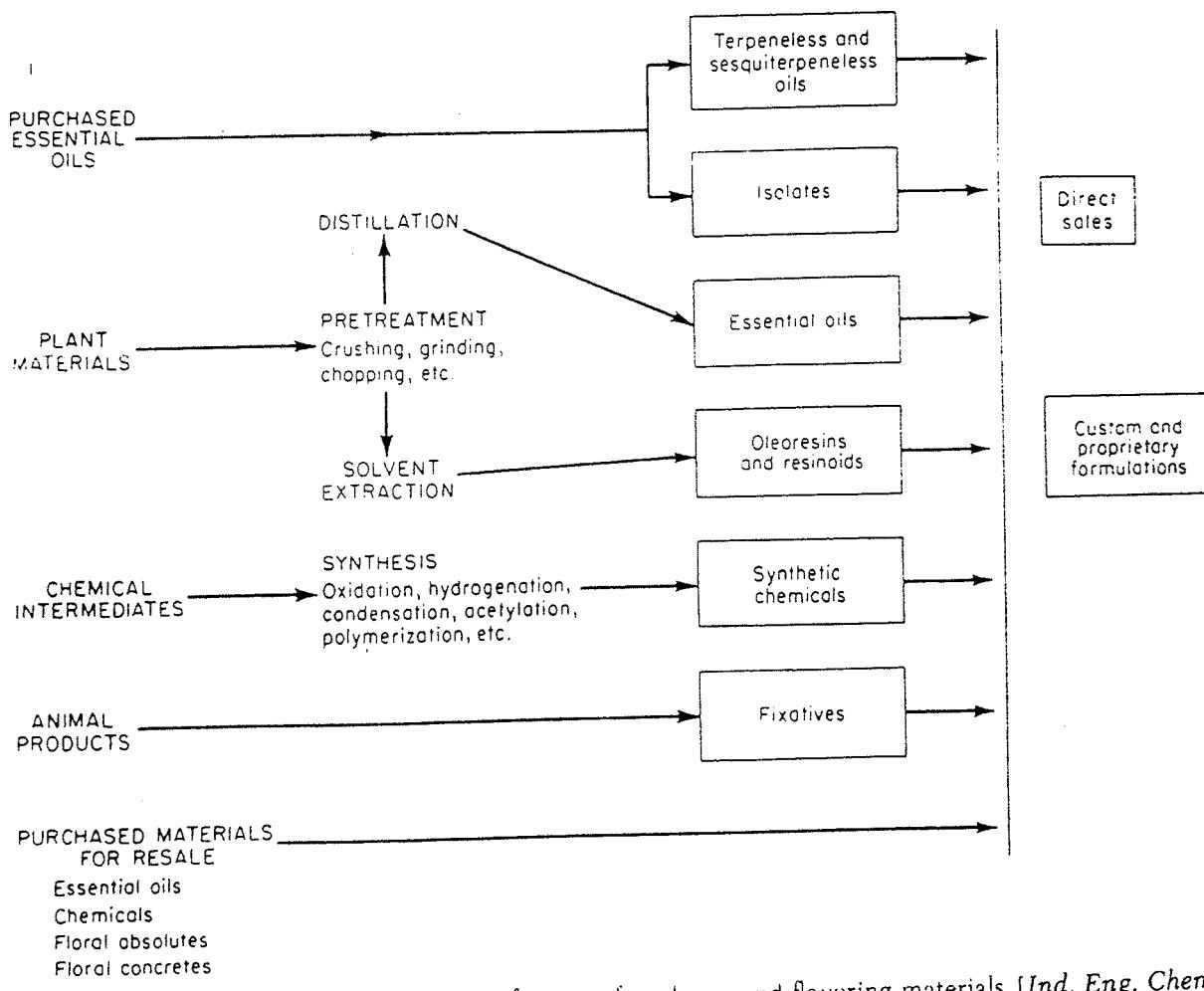
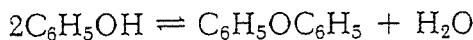


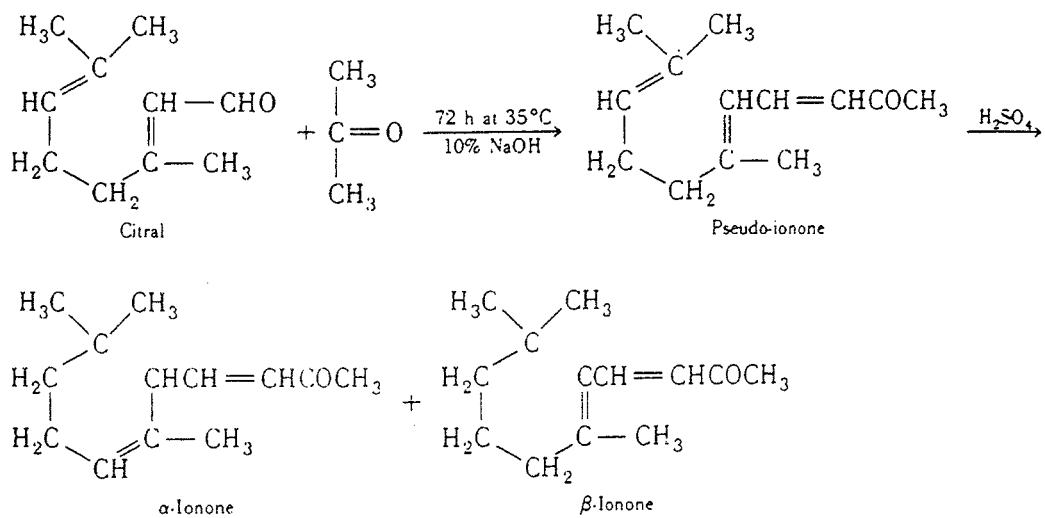
Fig. 1.1. Outline flowchart for the manufacture of perfume and flavoring materials. [*Ind. Eng. Chem.* 53 (6) 422 (1961); courtesy of Fritzsche Bros.]

material, or the Hassmann-Reimer synthesis, where coumarin-3-carboxylic acid is produced as an intermediate. Over 450,000 kg is produced per year.

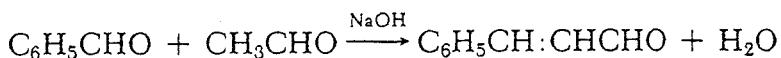
Diphenyl oxide, or *ether*, is largely used in the soap and perfume industries because of its great stability and strong geranium odor. Diphenyl oxide is obtained as a by-product in the manufacture of phenol from chlorobenzene and caustic soda.



Ionone and its homologs possess the so-called violet type of odor, thus constituting the base of violet perfumes. These compounds, however, are indispensable to fine perfumes, and there are but few which do not contain at least a small percentage of ionones. Annually, about 225,000 kg of ionones is produced. Because of the high price of the natural oil of violet, this was one of the first essential oils synthesized, although it has since been found in certain obscure plants. The olfactory properties of ionone are due to the presence of *dl*- α -ionone and β -ionone. Their manufacture involves two steps: First, the pseudo-ionone is prepared by the condensation of citral obtained from lemon grass oil. This is followed by an acid ring closure, and the commercial ionone is purified by distillation. Commercial ionones are generally mixtures with one form predominating, although separations are sometimes made through bisulfite compounds.



Cinnamic aldehyde has a cinnamon odor. As it oxidizes in air to cinnamic acid, it should be protected from oxidation. Although this aldehyde is obtained from Chinese cassia oils, it is synthesized by action of alkali upon a mixture of benzaldehyde and acetaldehyde (Fig. 27.2). The production is about 365,000 kg per year.



This and most other products for fragrances must be purified, for example, by vacuum fractionation (Fig. 27.3).

Esterification Processes. *Benzyl benzoate* has a faint aromatic odor, boils at 323 to 324°C, and is a fixative and a flavoring material. It occurs naturally in balsams (Peru, Tolu) but is prepared commercially by the esterification of benzoic acid with benzyl alcohol or by the Cannizzaro reaction with benzaldehyde.

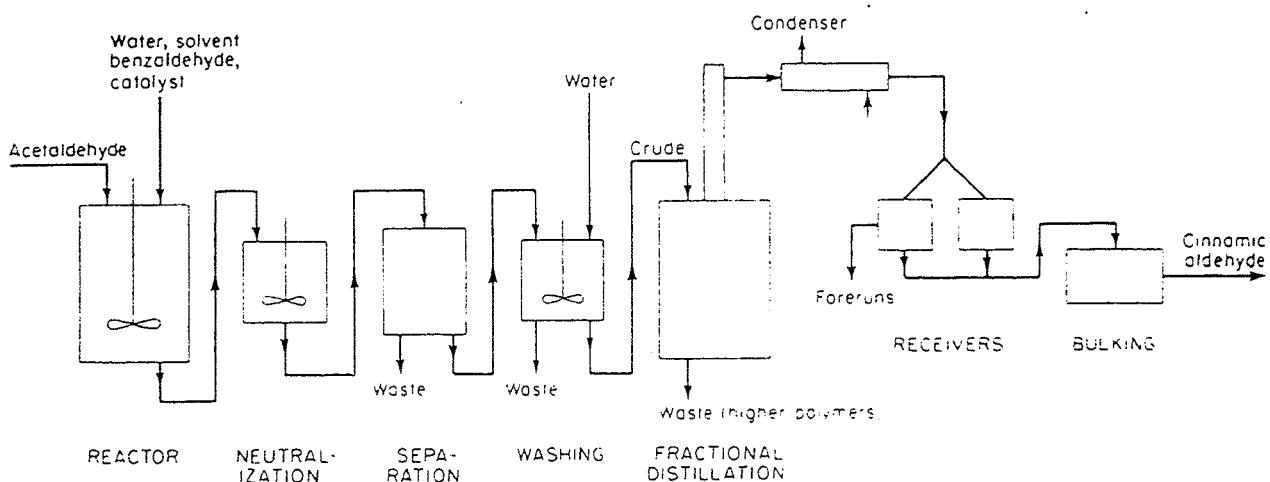


Fig. 1.2. Flowchart for cinnamic aldehyde production by aldol condensation. (Fritzsche Bros., Inc.)

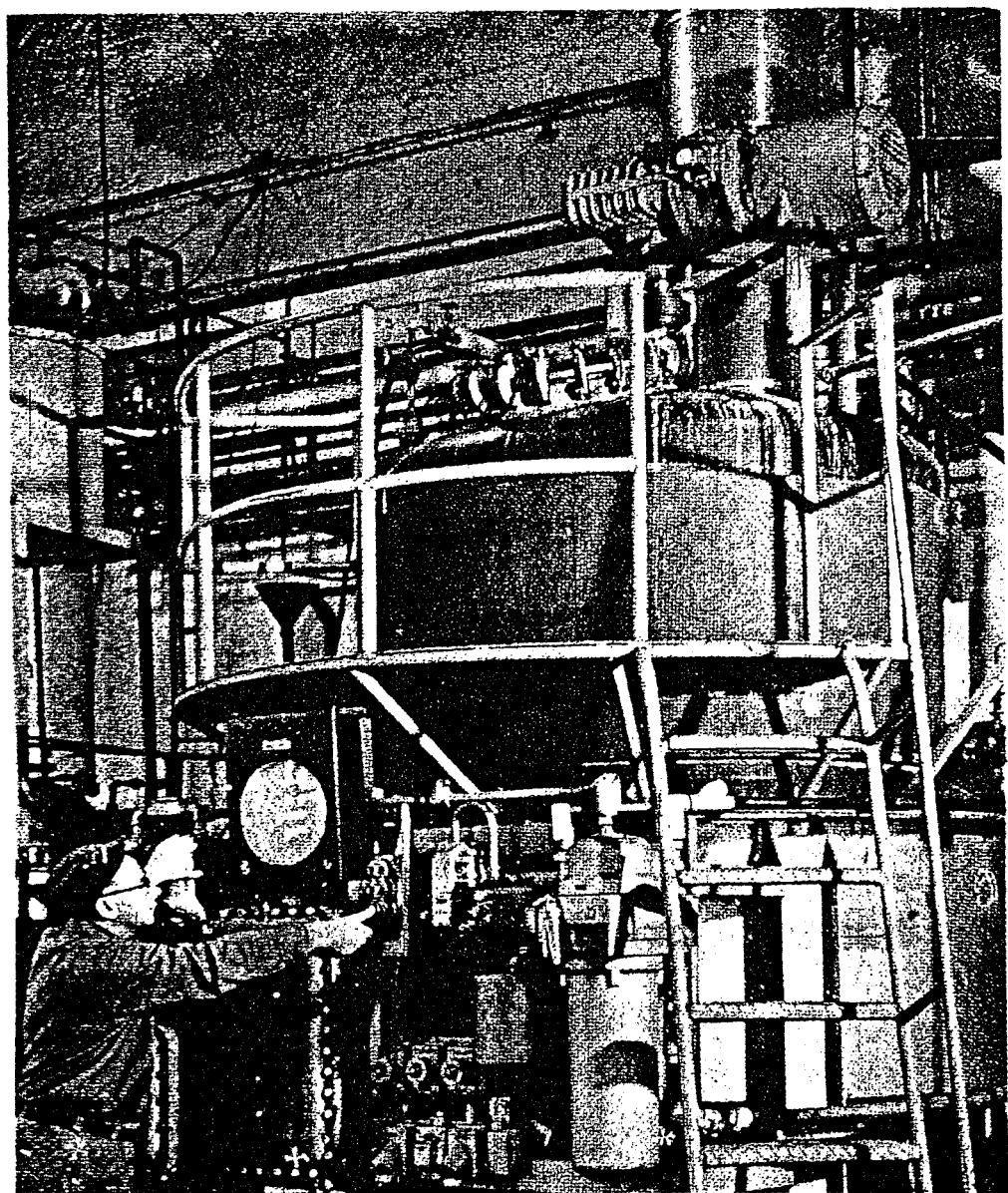
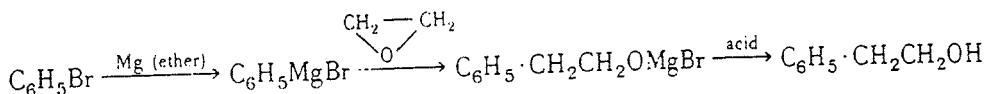


Fig. 1.3. High-temperature vacuum fractionating equipment. (Fritzsche Bros., Inc.)

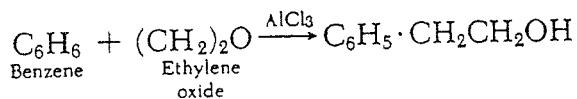
Two esters of *salicylic acid* (*o*-hydroxy benzoic acid) are very important commercially in the perfume and flavoring industries. About 160,000 kg of *amyl salicylate* is used annually in a variety of perfumes, because of its lasting quality and low price. About 1.8×10^6 kg of *methyl salicylate* (synthetic wintergreen oil) is consumed annually as a flavoring ingredient. These esters are prepared as follows: Carbon dioxide and sodium phenate are reacted under pressure to obtain the salt of phenylcarbonic acid. This salt is isomerized to sodium salicylate by heating to 120 to 140°C. The esters are made from the acid and the proper alcohol.

Benzyl acetate ($C_6H_5CH_2OCOCH_3$) is another widely used ester because of its low cost and floral odor. About 450,000 kg is sold annually for soap and industrial perfumes. It is prepared by esterification of benzyl alcohol, by heating with either an excess of acetic anhydride or acetic acid with mineral acids. The product is purified by treatment with boric acid and distilled, giving a purity of over 98%. Large amounts of *benzyl alcohol* are employed in pharmaceuticals, lacquers, etc. (about 1.8×10^6 kg per year). This alcohol has a much weaker odor than its esters. It is made by hydrolyzing benzyl chloride.

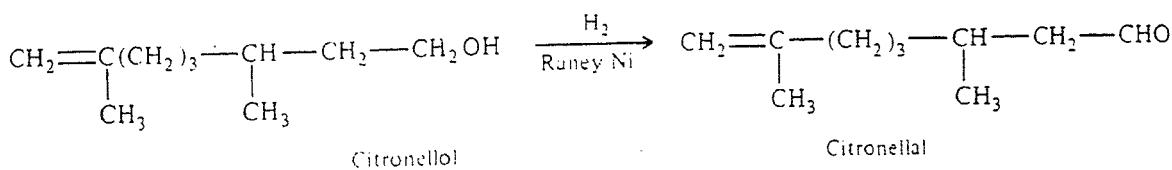
Grignard Processes. *Phenylethyl alcohol* has a roselike odor and occurs in the volatile oils of rose, orange flowers, and others. It is an oily liquid and is much used in perfume formulation, more than 450,000 kg being sold annually. *Phenylethyl alcohol* can be made by a number of procedures; the Grignard reaction is used generally:



However, the Friedel-Crafts reaction is outlined in the flowchart in Fig. 1.4 and follows the reaction

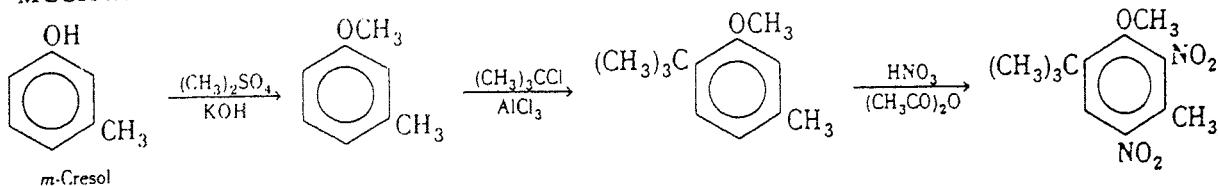


Hydrogenation. See Fig. 1.5 for citronellal from citronellol by Raney nickel hydrogenation at 1375 kPa.



Nitration Processes. *Artificial musks* comprise a number of products not identical with the natural musk, which derives its odor from macrocyclic compounds. Nitro musks are practical and economical substitutes for this expensive natural fixative, and more than 90,000 kg of musk xylene alone is manufactured annually. The reactions for the three important commercial artificial musks are

MUSK AMBRETTE



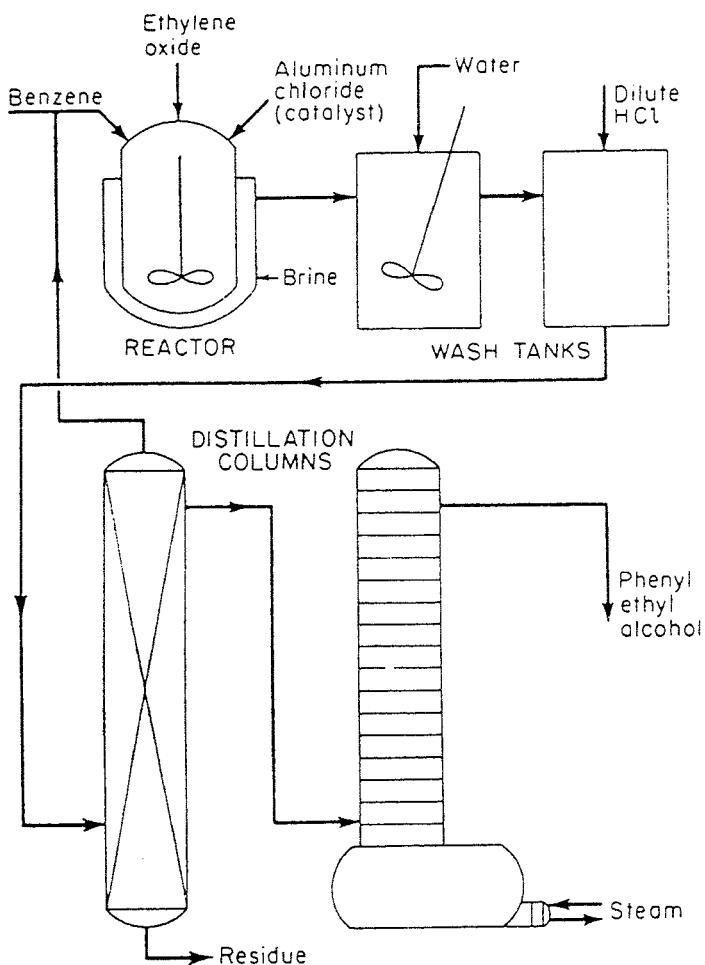
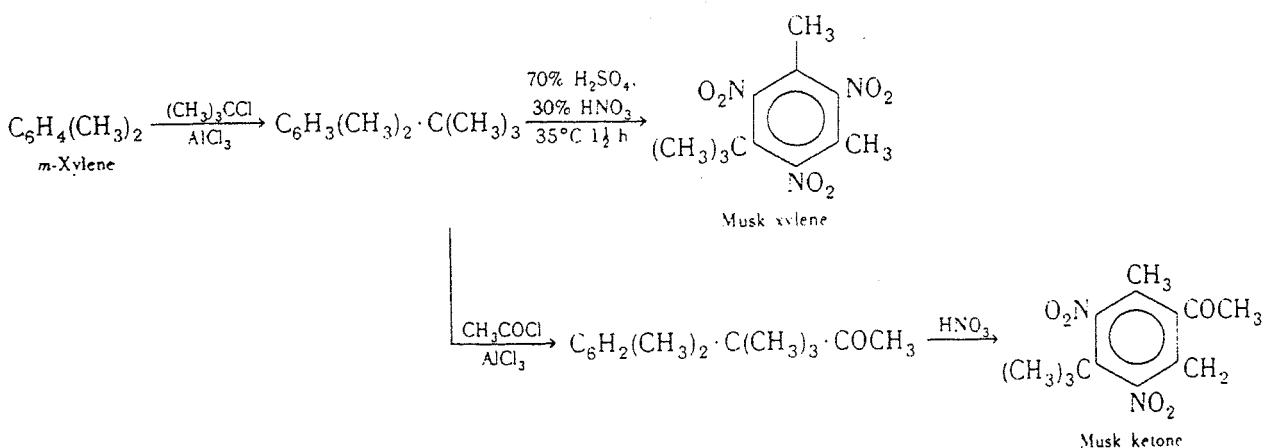


Fig. 1.4. Phenylethyl alcohol formed by the Friedel-Crafts reaction. [Chem. Eng. 65 (4) 113 (1958); courtesy of Van Amerigen Haebler.]

MUSK XYLENE AND MUSK KETONE



Oxidation Processes. Vanillin is one of the most widely used flavors, more than 680,000 kg/year being manufactured. It is used as a flavor in perfumery and for deodorizing manufactured goods. Many processes have been employed in its manufacture, such as the following:

1. From eugenol from oil of cloves, through isoeugenol, followed by oxidation to vanillin, using nitrobenzene as the oxidizing agent:

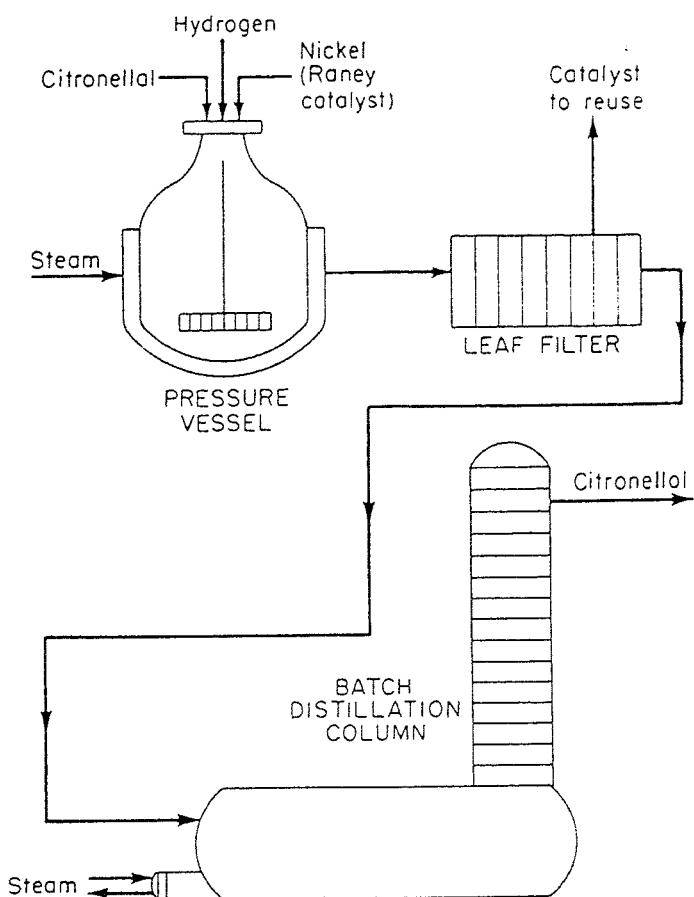
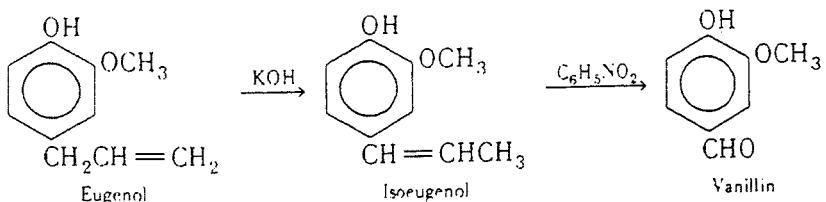


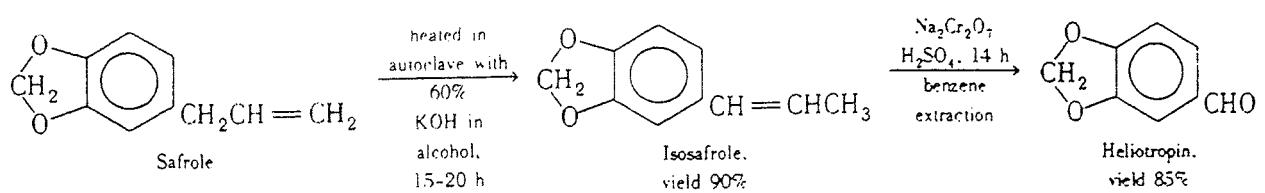
Fig. 1.5. Hydrogenation under pressure of 1380 kPa to convert citronellal to citronellol. [Chem. Eng. 65 (4) (1958); courtesy of Van Amerigen Haebler.]



2. From lignin⁸ through an alkaline pressure cook at 900 to 1400 kPa for $\frac{1}{2}$ to 1 h. The vanillin is purified through the sodium bisulfite compound and extraction with benzene or isopropanol (Fig. 1.6). Most of the vanillin on the market is made this way.

3. From phenol⁹ or *o*-chloronitrobenzene through guaiacol, following the usual synthetic procedure.

Heliotropin, or *piperonal*, has a pleasant aromatic odor resembling heliotrope. It is produced from safrole by the following reactions:



⁸Craig *et al.*, U.S. Patent 3,054,659 (1962); ECT, 3d ed., vol. 14, 1981, p. 306.

⁹Schwyzer, Die Fabrikation pharmazeutischer und chemischtechnischer Produkte, Springer, Berlin, 1931, pp. 205-209, 279-288.

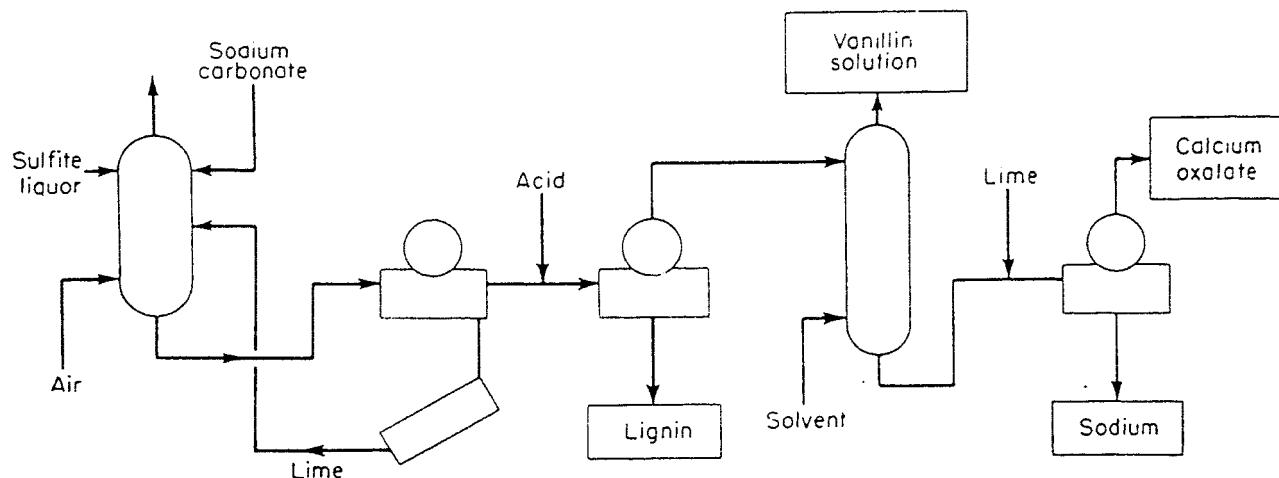
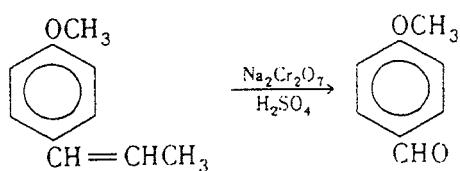


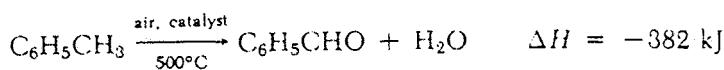
Fig. 1.6. Vanillin from lignin. [Chem. Week 89 (37) 103 (1961).]

Anisaldehyde is a colorless oily liquid with an agreeable odor resembling coumarin, which is developed only after dilution and in mixtures. It is made by the oxidation of anethole (the chief constituent of anise, star anise, and fennel oils). Anethole has been obtained recently in this country at very low cost from higher-boiling fractions of pine oil.



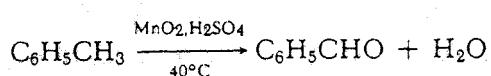
Benzaldehyde is used as a flavoring agent, as an ingredient in pharmaceuticals, and as an intermediate in chemical syntheses. Commercially, it is produced by several methods and in two grades, technical and refined. The technical grade is largely used as an intermediate in the synthesis of other chemicals, such as benzyl benzoate, cinnamic aldehyde, and dyes. Most of the technical grade is made by direct vapor-phase oxidation of toluene, although some is made by chlorinating toluene to benzal chloride, followed by alkaline or acid hydrolysis. For perfume and flavoring use, the refined, chlorine-free grade is required, which is economically produced by the direct vapor-phase oxidation of toluene. This oxidation is sometimes carried out in the liquid phase.

VAPOR PHASE



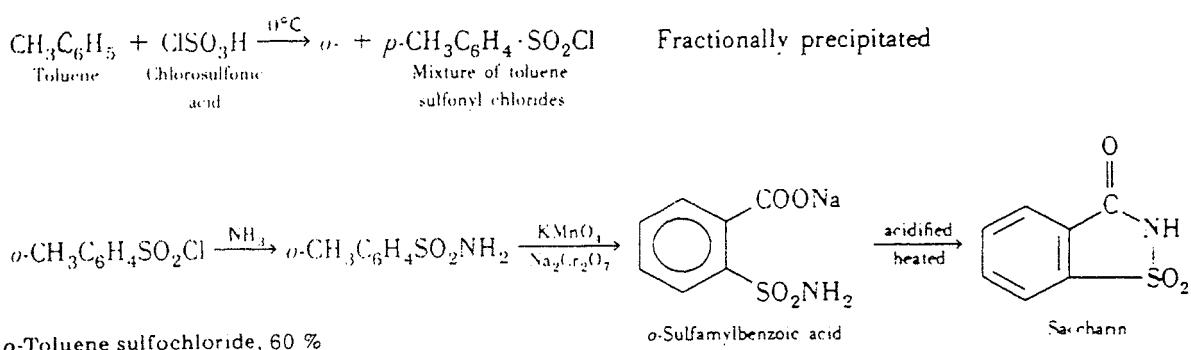
It is claimed that a catalyst mixture of 93% uranium oxide and 7% molybdenum oxide gives relatively high yields.

LIQUID PHASE

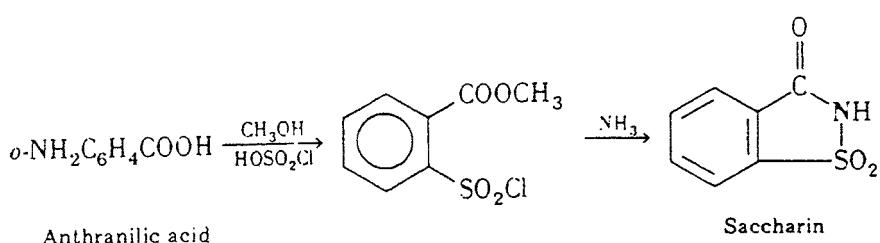


Saccharin USP (o-benzosulfimide) is approximately 500 times sweeter than sugar. It has been widely used by diabetics and in diet drinks and foods. However, in 1972 the FDA

removed saccharin from the Generally Recognized as Safe (GRAS)¹⁰ list and required that all food and beverages containing saccharin have a warning label. A study was undertaken by the National Academy of Sciences to determine its safety for human consumption, but it did not provide definite conclusions.¹¹ In 1977 the FDA restricted the use of saccharin, a decision based on limited test data on laboratory animals. Saccharin is manufactured, employing the following reactions, with a 90 percent yield on the last step.



An alternate synthesis from anthranilic acid is claimed to yield a product with less bitter aftertaste.



Miscellaneous Processes. Aspartame,¹² 1-aspartyl-1-phenylalanine, is 200 times sweeter than sugar. It has recently won limited approval from the FDA for use in some foods, and for use in soft drinks. It now is able to compete in the nonnutritive sweetener market with saccharin, which has been on the market for many years.¹³ The regulation that requires a warning label on saccharin-containing foods will expire in 1983, and, unless it is extended, aspartame will be the only accepted nonnutritive sweetener on the market. Saccharin consumption is about 7 g per capita per year, and $3 \text{ to } 4 \times 10^3 \text{ t/year}$ is produced, so the market is large.^{13a} A combination of saccharin and aspartame is sweeter than either compound alone and aspartame has no objectionable aftertaste as saccharin does. Aspartame, however, is not very stable to heat and liquids, but it will retain its sweet taste in soft drinks for about 6 months.

Terpineols are among the cheapest synthetics and are widely used in soap because of their woodsy and floral odors. Formerly, all terpineols were made from turpentine oil, which consists largely of α -pinene, but recently pine oil has become an important source. Terpineols

¹⁰Hall, GRAS—Concept and Application, *Food Technol.* **29** (1) 48 (1975).

¹¹National Academy of Science Report No. PB-238137/AS, 1975 (available from National Technical Information Service, Springfield, Va.).

¹²For saccharin and aspartame, *Food Eng.* **54** (7) 77 (1982).

¹³Sugar Substitutes Seek Sweet Smell of Success, *Chem. Eng. News* **52** (44) 37 (1974), *Food Eng.* **46** (8) 27 (1974).

^{13a}t = 1000 kg.

may be manufactured directly in a one-step process from pinene by reaction with sulfuric acid and acetone for 6 h at 35 to 40°C. The product is purified by fractional distillation. The two-step method has an advantage in that the purification of the intermediate, terpin hydrate, is easier than that of terpineol. Terpin hydrate is formed by reacting pinene with dilute sulfuric acid and an emulsifying agent. The purified hydrate is dehydrated to terpineol by oxygenated carboxylic acids. Terpineols are separated from pine oil by fractional distillation.

Menthol has long been extracted as the levo from oil of Japanese peppermint and used in cigarettes and many other products as an antiseptic cooling flavor. The pure optically active form is made by Glidden Co. from β -pinene (from turpentine).¹⁴ This compound is hydrogenated, isomerized, and dehydrogenated to make β -citronellal. Catalytical conversion produces isopulegol, and hydrogenation yields *l*-menthol, after fractional distillation and crystallization.

The acetals of aldehydes have an odor only slightly modified from that of aldehydes but have great alkali resistance. Hence these acetals are used in soaps, which are very difficult to perfume.

Perfume Formulation

An actual example of a compound perfume similar to a widely sold product (Table 1.2) indicates the various components that have been discussed and shows their use in a blended product. The foundation odors are from eugenols, methyl ionone, and bergamot oil. Although the formulation given in the table shows a lower number, a single fragrance may contain 50 to 100 different compounds and subcompounds; in fact, as many as 300 ingredients may be used. Approximately 500 natural and 3000 synthetic oils are available for perfume production.¹⁵

FRAGRANCE QUALITY. The majority of domestic perfume houses do not manufacture their own scents; they usually import natural floral oils and have their synthetics custom-made by

¹⁴Chemicals from Trees, *CHEM TECH* 5 (4) 235 (1975).

¹⁵Aerosols; Fragrance Front-Runners, *Chem. Week* 86 (1) 24 (1960).

Table 1.2 Composition of a Perfume

Component	Grams	Component	Grams
Essential oils		Synthetics	
Sandalwood oil	10	Coumarin	27.5
Bergamot oil	117.5	Vanillin	20
Ylang-ylang oil	40	Benzyl acetate	30
Petigrain oil	10	Oleoresin, opopanax	2.5
Orange flower oil	10	Balsams (resinoids)	
Rose otto	15	Tolú	5
Jasmine absolute	20	Peru	7
Isolates		Benzoin	70
Eugenol (from clove oil)	90	Animal fixative, castor tincture 1:10	12.5
Santalol (from sandalwood)	15	Synthetic fixatives	
Semisynthetics		Musk ketone	32.5
Isoeugenol (from eugenol)	110	Musk ambrette	12.5
Heliotropin (from safrole)	15	Vehicle, ethyl alcohol	450 kg
Methyl ionone (from citral)	237.5		

Table 1.3 Types of Perfumes

Classification	Manufacturer	Trade Name
Straight floral	Coty	Muguet des Bois
Floral bouquet	Revlon	Charlie
Aldehydic floral	Chanel	Chanel #5
Oriental	Coty	L'origon
Chypre	Factor	Acquamarine
Woody	Jovan	Sport Scent
Green	Shulton	Old Spice Herbal
Citrus	Jovan	Eau Fresh
Cougere	Dana	20 Carats
Canoe	Faberge	Brut
Musk	Jovan	Musk Oil
Spice	Shulton	Old Spice

aromatic firms. As the perfumer's skill and resources increase with experience and research, new equipment is developed for identifying fragrance components, even in trace quantities, such as infrared and ultraviolet spectrographs and chromatographs. Eventually, such instrumentation will be perfected to expedite production, but currently the perfumer's nose is regarded as the more discriminatory in arriving at a creative blend of exotic ingredients. Even he or she does not know precisely what will make one formulation successful where several hundred others may fail. Furthermore, after months of trial to attain certain objectives, a consumer panel may be unenthusiastic about the product. High quality from batch to batch is routinely ensured by standard tests, such as specific gravity, optical rotation, refractive index, acid number, and ester number. Provided success is met thus far, "the name, the package, the advertising must all be perfectly orchestrated" with the product.

The psychological effect of odor is successfully used primarily to increase customer appeal. Perfumed merchandise outsells its odorless counterpart by a large margin. An insurance company increased its sales of fire insurance overnight by sending out advertising blotters treated to simulate the acrid odor of a fire-gutted building. All kinds of paper are now perfumed to increase sales appeal. Table 1.3 lists the main types of perfumes.

THE FLAVORING INDUSTRY

There are only four basic flavors which the nerve endings in the taste buds on the tongue can detect: *sweet*, *sour*, *salty*, and *bitter*.¹⁶ The popular conception of flavor, however, involves the combination of these four basic stimuli with concurrent odor sensations. Apple, for instance, tastes merely sour, with a trace of bitterness from the tannins present. The main concept received of an apple is due to the odor of acetaldehyde, amyl formate, amyl acetate, and other esters present in the volatile portion. The principles of perfume blending also hold good for flavor manufacturing. The best flavoring essences are natural products altered and reinforced where necessary by synthetics. In addition to alcohol as a vehicle, glycerin and isopropyl alcohol are used for liquid preparations, and emulsions of bland gums, such as tragacanth and acacia (gum arabic), for pastes. The same fixatives are employed, especially vanillin and coumarin; animal types are used sparingly. Many essential oils find application

¹⁶Hornstein and Teranishi, The Chemistry of Flavor, *Chem. Eng. News* 45 (32) 93 (1967).

in the flavor industry, the more common being spice oils, citrus oils, peppermint, and spearmint. Almost all perfume synthetics find acceptance, plus a number made especially for flavors. The esters of ethyl, methyl, amyl, propyl, and benzyl alcohols with acetic, propionic, butyric, salicylic, caproic, formic, valeric, and anthranilic acids are widely used to characterize fruit flavors. As with flower perfumes, many chemical specialties keynote individual fruit aromas. The γ -lactone of undecylenic acid is a true representation of the fresh odor of a cut peach. A strawberry base is the ethyl ester of methylphenylglycidic acid, although it is not a true effect and partakes of a somewhat unnatural tone. Anethole has the taste of anise and licorice, benzyl acetate tastes like raspberry or cherry, and allyl caproate is used for pineapple flavors. Other common compounds used for flavorings are cinnamaldehyde (cinnamon), diacetyl (butter), menthol (mint), and isoamyl acetate (banana).

Natural Fruit Concentrates

Although the essential oils used in flavoring are the same grade and source as those used for perfumes, fruit flavors are handled in a somewhat different manner. Because of the large percentage of water in most common fruits (from 75% in the banana to 90% in the strawberry) and the presence of considerable amounts of sugar and other easily fermented materials, special processes must frequently be employed, such as the following:

Distillation and extraction of the fruit. The ripe fruit is stoned and comminuted. It is then subjected to steam distillation and rectification until all the aroma is concentrated in a small portion of the aqueous distillate. This portion is then extracted with low-boiling petroleum ether, and the ether removed under vacuum to leave an *essence*, or *quintessence*, of the fruit used. Cherry, apple, strawberry, and raspberry are treated by this method.

Extraction of the juice. In this system the expressed and filtered juice is extracted directly without previous distillation. Occasionally, the juice is allowed to ferment slightly before extraction. This is supposed to result in a fuller flavor.

Concentration of the juice. The expressed and filtered juice is concentrated in vacuum evaporators with a low degree of heat until the water is largely driven off and the sugar concentration is high enough to inhibit bacterial growth (60%). This type of concentrate often has a "jam," or cooked flavor, especially in the case of the strawberries. An alternative method of concentration is freezing. After reducing the temperature sufficiently, the mush of practically pure water ice is filtered off, and the partly concentrated juice is refrozen and refiltered until the requisite strength is obtained. This is the *optimum* method of producing concentrates, since there is little injury from heat, and the slight off-flavors from oxidation can be avoided by running the process in an atmosphere of carbon dioxide.

VANILLA. The vanilla bean is grown principally in Madagascar, Tahiti, and Mexico. It is the immature fruit of the orchid *Vanilla planifolia* and is cultivated as a vine on trees which support it. The pods are picked when they are just starting to turn from a uniform green to yellow at the tip and have a rather disagreeable odor. The green pods undergo a curing treatment of from 3 to 5 months' duration. The cured bean is pliant, shiny, and dark-colored. The odor has become full and rich, and the treatment may have left white aromatic crystals on the outside of the bean. What has happened is that the glucoside glucovanillin, present in the bean, has been acted upon by a ferment and split into glucose, vanillin, and other aromatics. Substances identified in the vanilla bean are anisic acid, alcohol, and aldehyde; vanillic acid and alcohol; cinnamic acid and its esters; vanillin, ethyl vanillin, and possibly other homologs of vanillin.

Preparation of vanilla extract. One hundred pounds of a blend of Mexican and Bourbon beans is finely cut up and macerated cold, with three successive portions of 35% ethyl alcohol of 45 kg each. These extracts are combined to make a fine vanilla extract. Other solvents may be used, and the extraction carried further, but the product is coarser and less desirable as a fine flavor (cf. Fig. 1.6).

CHOCOLATE AND COCOA. The cacao bean, the seed of *Theobroma cacao* L. grows in equatorial areas on the tree in pods with from 30 to 60 beans. The pods are split open, and the watery pulp containing the seeds is allowed to ferment in boxes from 2 to 7 days, which, in addition to liquefying the pulp, kills the embryo (46°C), reduces the toughness of the bean, frees theobromine from the glucoside, and reduces the astringent tannin content. This fermentation is necessary for flavor in the final product. The fermented beans are dried and shipped to manufacturing centers. The beans are then heated in rotary roasters between 105 and 120°C, which develops the true chocolate flavor and aroma, removes unpleasant tannins and volatile matter (butyric and acetic acid, organic bases, and amines), dextrinizes the starch, and embrittles the husk. The roasted beans are quickly cooled to prevent overroasting, cracked in a conical mill, dehusked by a winnowing air stream, and degernminated. This product is known as *cacao nibs*. To work up the cacao product into chocolate, the modern method is to grind sugar in a closed-circuit disintegrator and the nibs in a separate water-cooled two-stage disk mill with closed-circuit removal of the fines. The two are then mixed. This method produces a fine, uniform product. The paste is run through a concher, which is a granite bed with reciprocally acting granite rollers. It reduces the particle size to an average of less than 1 μm . It is steam-heated to run at 57°C or can be allowed to heat itself by friction (50°C). Milk chocolates are prepared by adding condensed fresh milk or milk powder to the mill (melangeur). The finished product has a cocoa-butter content of 30 to 35% and not less than 12% milk solids. For cocoa, the roasted and ground beans are subjected to pressure in hydraulic presses to remove some of the fat content. Whereas originally roasted beans contain 55% fat, the product remaining after this treatment has the fat reduced to 20%, and is known as *cocoa*. The removal of fat makes a beverage that is not too rich and one in which the fat does not separate on top.

MONOSODIUM GLUTAMATE [MSG, $\text{COOH}(\text{CH}_2)_2\text{CH}(\text{NH}_2)\text{COONa}$]. This compound is an important flavoring agent, yet has no flavor of its own. It accentuates the hidden flavors of food in which it is used. Reports that the use of MSG in foods is harmful were denied by a National Academy of Science—National Research Council report in 1971.¹⁷ In 1974 the Food and Agricultural Organization of the World Health Organization approved the use of MSG as safe. Glutamic acid exists in three forms, but only the monosodium salt of L-glutamic acid has a flavor-accentuating capacity. Although glutamic acid is a constituent of all common proteins, the economical sources have been wheat gluten, corn gluten, and Steffens filtrate. When Steffens beet-sugar wastes are used, the principal steps involved are (1) concentration and collection of the Steffens filtrate, (2) its hydrolysis, usually with caustic soda, (3) neutralization and acidification of the hydrolysate, (4) partial removal of the inorganic salts, and (5) crystallization, separation, and purification of the glutamic acid. MSG is made from the acid as described above. The present production of MSG is largely from fermentation,¹⁸ and a

¹⁷Chem. Eng. News 49 (28) 17 (1971).

¹⁸New Processes, Chem. Eng. 69 (16) 17 (1962); Ind. Eng. Chem. Annual Unit Processes Reviews: Fermentation, from 1961 on; Hoelscher, Fermentation, Chem. Eng. 71 (8) 91 (1964); ECT, 3d ed., vol. 2, 1978, p. 410.

flowchart is presented in Fig. 1.7. Several U.S. companies have developed their own microbiological process or obtained it from the Japanese. The raw material is frequently dextrose or sugar. However, the Japanese are using a synthetic process based on acrylonitrile

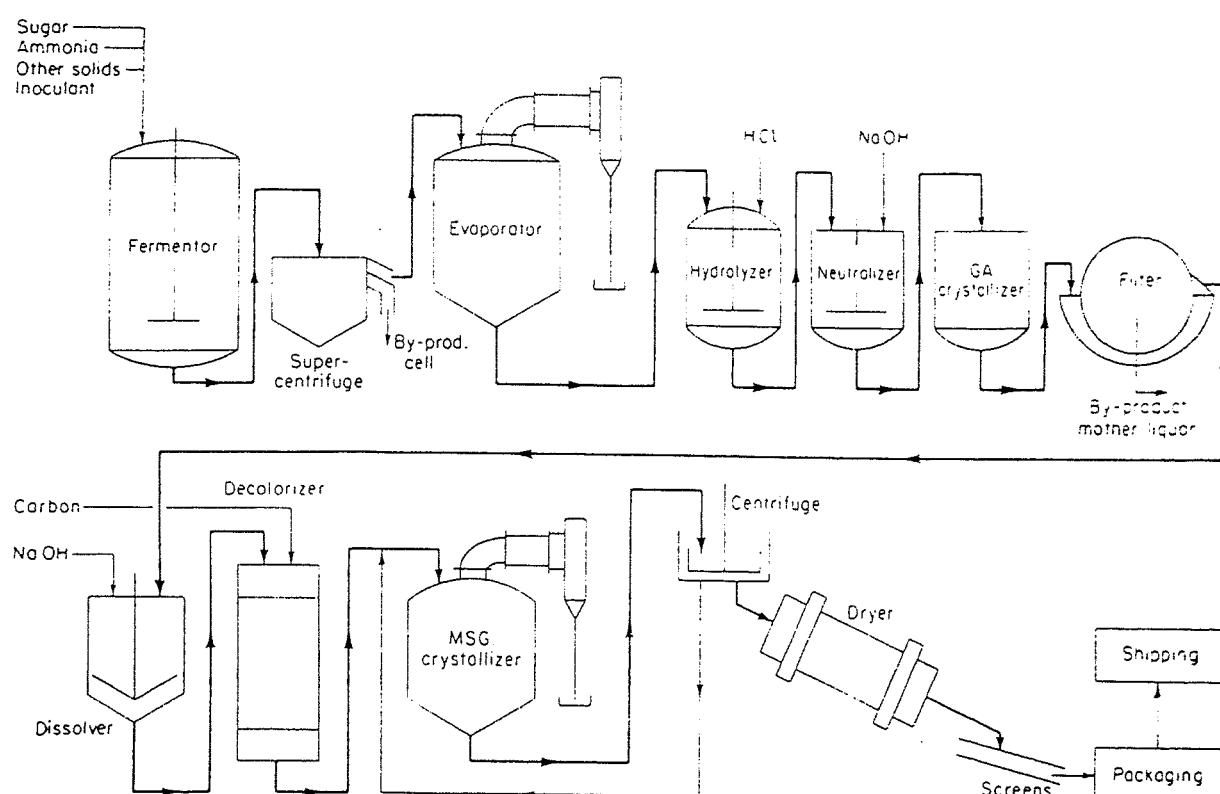
Flavor-Essence Formulation¹⁹

Formulas are given in Table 1.4 for a fruit flavor used in gum manufacture and a natural apricot flavor. These show how a well-balanced flavor may be made up of natural products reinforced with suitable synthetics as well as a wholly natural formulation. Many formulas are to be found in print which consist mainly of esters of synthetic origin. These are harsh and unnatural, and, in many cases, the only resemblance to the original is in the designation of the flavor.

FOOD ADDITIVES

"The food revolution in progress since the turn of the century almost defies description. The evidence is all around us—on fertile farm lands, and in lush orchards, among grazing herds

¹⁹Mussinan, Analytical Chemistry and Flavor Creation, *CHEMTECH* 10 (10) 618 (1980).



To produce 1 t of $\text{MSG} \cdot \text{H}_2\text{O}$, the following materials and utilities are required:

Sugar	1.5–2.5 t	Fuel	46.4 MJ
Electricity	79,200 MJ	Direct labor	17.6 work-h

Fig. 1.7. Flowchart of monosodium glutamate production by fermentation. (International Minerals and Chem. Corp.)

Table 1.4 Typical Flavors

Artificial Fruit Flavor for Chewing Gum			
	%		%
Heliotropin	0.05	Oil of lemon	5.00
Ethyl vanillin	1.00	Oil of tangerine	5.00
Vanillin	2.00	Ethyl acetate	16.40
Aldehyde C ₁₆	0.55	Ethyl butyrate	15.00
Oil of cloves	1.00	Isoamyl acetate	10.00
Oil of peppermint	2.00	Isoamyl butyrate	5.00
Oil of orange	37.00		

Natural Apricot Flavor			
	%		%
Apricot juice conc.	99.6	Oil of orange	0.1
Absolute carob	0.1	Oil of petitgrain	0.05
Vanilla extract	0.1	Oil bitter almond	0.05

and loaded refrigerator trucks and railroad cars, in magnificent food stores and, finally, in kitchens and on dining tables at home or in restaurants.²⁰ The food industry, estimated at over $\$200 \times 10^9$ yearly, is the country's *largest business*. The average family spends approximately 18 percent of its income on food. (See Chap. 25, Food and Food By-Product Processing Industries, for details on the size of this industry.) Food additives are those chemicals combined with foods by the manufacturer to effect certain modifications involving preservation, color, flavor enhancement, and stabilization, which have helped to make an astounding improvement in our food supply, as well as alleviating work in the kitchen. Additives are as old as history itself, spices, for example. *Intentional additives* are substances added in carefully controlled amounts to preserve the quality of food, improve its nutritive value, or add flavor, for example, MSG (Fig. 1.7). Common kitchen staples such as vinegar, starch, and salt are in this category. *Incidental additives* are those that, although having no function in finished food, become part of it through some phase of production, processing, storage, or packaging.

The food additives have been separated into 52 categories.²¹ This list ranges from acidulants, anticaking (drying) agents, baking aids (yeast foods) through flavors, flavor enhancers, starch modifiers, nonnutritive sweeteners to preservatives, sequestrants, chelating agents, stabilizers, vitamins, and wetting agents. The main classifications²² are colors, 3 percent; flavors, 16 percent; enzymes, 8 percent; acidulants, 8 percent; nonnutritive sweeteners, 2 percent; surfactants, 10 percent; antioxidants, 3 percent; preservatives, 4 percent; flavor enhancers, 7 percent; vitamin supplements, 3 percent; and nonspecialty additives such as soy concentrates, carrageenin, alginates, and leavening agents, 36 percent.

Commonly used additives include chemical preservatives like propionic acid and benzoic acid; buffers and neutralizing agents, such as acetic acid and sodium citrate; emulsifying

²⁰Food Additives Codex, 1972, Manufacturing Chemists Association; Furia, *Handbook of Food Additives*, Chemical Rubber, Boca Raton, Fla., 1968; Fernandez, *Mixing Technology and Food*, New Eng. 3 (11) 52 (1974); ECT, 3d ed., vol. 11, 1980, p. 146.

²¹Food Ingredients Directory, Intechmark Corp., Palo Alto, Calif.

²²Another Checkup for Additives, *Chem. Week* 127 (17) 29 (1980).

agents like polysorbates; nonnutritive sweeteners, such as saccharin; nutrients, among which are ascorbic acid and other vitamins; and thickeners like agar-agar and acacia. Here should be included spices like allspice and ginger and, finally, essential oils (Table 1.1) such as bitter almond and lemon. Some of these additives are permitted to be used freely, and others in limited amounts.

The FDA is conducting an on-going review of the GRAS list of substances. Contrary to popular reports, governmental regulation concerning safety in food products is not completely biased on the side of the food industry.

It is useful in gaining perspective on the use of food additives to realize that the average person consumes 680 kg of food per year, and of that only 63 kg are food additives. Of the 63 kg, 58.5 kg are composed of sugar, salt, corn syrup, and dextrose which are all normal, natural foods.²³ Leavening agents or substances used to adjust the acidity account for 4 kg, which leaves only about 0.5 kg of other additives. These are divided among about 1800 different substances. Food additives play an invaluable role in preserving food and add greatly to its variety, stability, flavor, abundance, and appearance. For any new food additive the FDA requires submission of a Food Additive Petition (FAP) which must contain documented information on safety, declaration of intended use(s), efficacy at specific levels in the food system, manufacturing details including intermediates, and an environmental impact statement. It has been estimated that it can easily cost \$1 million just to obtain FDA approval. Because of this high cost, less than a dozen new products have been approved in the last 20 years. Most of the additives used have been approved for years, but the FDA is currently engaged in requiring the retesting of many of them.

NATURAL ACCESSORY CHEMICALS. Foodstuffs contain small amounts of accessory chemicals, including vitamins (Chap. 6), chelating agents, and natural antioxidants. Carbohydrates consist of various sugars, starches, dextrins (Chap. 30), celluloses, and gums. Proteins are composed of amino acids. Shortenings contain esters of palmitic, oleic, linoleic, and stearic acids. Natural foodstuffs contain substances of no known nutritive value, as well as substances that are harmful if taken in larger amounts than are normally used; for example, coffee and tea contain caffeine, whose pharmacological effect is well known. Even small amounts of arsenic and other toxic metals are found in food.

Potatoes contain so much solanine (a deadly poison) that if the amount consumed by the average person in a year was concentrated into a single dose, it would be sufficient to kill a horse. The list could be extended greatly, but it is sufficient to realize that "natural" foods are not necessarily better or safer than properly prepared food containing carefully tested and controlled additives.

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²³If It's Natural, How Good Is It? *Food Eng.* 54 (3) 7 (1982).